

Theory of Gel Formation

Drop-wise Addition of $R-A_f$ solution onto $R-B_g$ Solution

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Abstract

A theory of drop-wise addition polymerization is developed. Because of the linear growth of the reaction volume V , the system gives rise to a new type of distribution function for cyclic species that can be expressed by the sum of two terms: the conventional distribution term and a extra term due to the dilution effect. The present result is an extension of the conventional homogeneous polymerization that corresponds to a special case without the extra term. Making use of the result we derive the gel point formula for this unique polymerization. The theoretical result is compared with the recent observations.

Key Words: Drop-wise Addition/ Distribution of Cyclic Species/ Gel Point

1 Introduction

Organic chemists often make use of the technique of the drop-wise addition. When the synthesis of macrocyclic compounds is designed, the drop-wise addition has been employed frequently: *'Together with use of a large amount of solvents a technique is introduced that a reagent is added slowly keeping the system in high dilution, since the molecule is more likely to react with itself than with other molecules in high dilution.'* In contrast, the same technique has rarely been employed in polymer chemistry where constructing intermolecular bonds in longer sequence is necessarily required; intramolecular bonds simply waste valuable functional units, thus giving useless, unwelcome cyclic by-products.

Quite recently an interesting synthetic architecture of the drop-wise addition polymerization was put forth by Turkish group [1]. It has been known earlier that aliphatic isocyanates ($-NCO$) react with aliphatic amines ($-NH_2$) more than one thousand times faster than with alcohols ($-OH$). Making full use of this velocity difference between amines and alcohols, Yilgor and coworkers investigated the polymerizability of diisocyanates and diamines in isopropyl alcohol (IPA). Typically an IPA solution of a diisocyanate and that of a diamine are prepared separately; the diamine solution is introduced into the reaction vessel and the diisocyanate solution the addition funnel; then the diisocyanate solution is slowly added drop-wise onto the diamine solution. They found that the reaction is very fast at room temperature and yields clear and homogeneous polymer solutions of high molecular weight.

To date no theoretical treatment has been put forth for the drop-wise addition polymerization. The purpose of this paper is to construct the theory for this interesting polymerization. First we discuss the molecular size distribution of linear polymers without rings using kinetic arguments, then extend the result to the branched polymers. It has been shown that the size distribution for tree clusters can be derived beautifully by the statistical-mechanics approach [2]. In order to gain deep insights into the drop-wise addition polymerization, however, the kinetic treatment is essential and is found to be powerful. We show that the resultant distribution function is equivalent to that of the multiple link system [3]. Next we derive the size distribution of cyclic species, showing that because of the continuous change of the system volume in the drop-wise addition polymerization, a new type of distribution function arises. Making use of the result together with the known formalism [4], finally we derive the gel point equation. The theoretical result is compared with recent observed data.

2 Theoretical

The basic assumption of the drop-wise addition polymerization is that

1. a solution of $R-A_f$ molecules is added drop-wise into a solution of $R-B_g$ molecules;
2. the velocity of reaction is sufficiently slow so that the complete mixing is achieved before the reaction starts; as a result the principle of equireactivity is fulfilled;

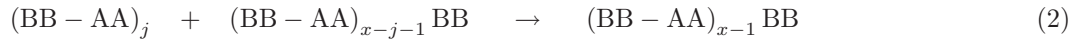
quite conversely

3. the velocity of reaction must be sufficiently fast in the time scale of the dropping interval (δu), so that all the $R-A_f$ molecules contained in one droplet must be consumed completely forming $A-B$ bonds within δu . As a result the system is always comprised of the $(BB-AA)_n$ BB type molecular species alone (n represents the number of $R-A_f$ molecules and $n = 0, 1, 2, \dots$).

2.1 Ideal Drop-wise Addition Polymerization

We consider the limiting case that each droplet contains only one molecule; namely, a *single* $R-A_f$ molecule is added drop-wise onto the solution of the $R-B_g$ monomers.

Consider the transition from u to $u + \delta u$ drops ($\delta u = 1$). In this minute interval, the following set of elementary reactions should occur.



with $x = 1, 2, 3, \dots$. Eq. (2) (intermolecular reaction) competes with eq. (3) (cyclization reaction). An essential point is that the above set of reactions (1)-(3) must be completed within δu . So these reactions constitute a unit chemical cycle. The drop-wise addition polymerization proceeds repeating this cycle.

2.1.1 Molecular Size Distribution in Linear Process

First consider the linear system without rings. Let M_B denote the total number of the $R-B_g$ units in the system. Let BA_x and BB_{x-1} be the abbreviations of the molecular species, $(BB-AA)_x$ and $(BB-AA)_{x-1}BB$, respectively. Then their variations are for eq. (1)

$$\delta N_{BA_x} = \frac{2N_{BB_{x-1}} \cdot 2N_{AA}}{2M_B(1-D_B) \cdot 2N_{AA}} \quad \text{for } (BB-AA)_x, \quad (4)$$

$$\delta N_{BB_{x-1}} = \frac{-2N_{BB_{x-1}} \cdot 2N_{AA}}{2M_B(1-D_B) \cdot 2N_{AA}} \quad \text{for } (BB-AA)_{x-1} BB, \quad (5)$$

and for eq. (2)

$$\delta N_{BB_{x-1}} = \frac{\sum_{j=1}^{x-1} \delta N_{BA_j} \cdot 2N_{BB_{x-j-1}} - 2N_{BB_{x-1}} \sum_{k=1}^{\infty} \delta N_{BA_k}}{2M_B(1-D_B) \sum_{k=1}^{\infty} \delta N_{BA_k}}. \quad (6)$$

By the definition of the ideal drop-wise addition, $N_{AA} = 1$ and $\sum_{k=1}^{\infty} \delta N_{BA_k} = 1$. Combining eqs. (4) and (5) with eq. (6), we have

$$\delta N_{BB_{x-1}} = \frac{\sum_{j=1}^{x-1} \left\{ \frac{N_{BB_{j-1}}}{M_B(1-D_B)} \right\} \cdot 2N_{BB_{x-j-1}} - 4N_{BB_{x-1}}}{2M_B(1-D_B)} \delta u. \quad (7)$$

Eq. (7) may be recast in the familiar form:

$$\delta N_{BB_{x-1}} = \frac{\frac{1}{2} \sum_{j=1}^{x-1} N_{BB_{j-1}} N_{BB_{x-j-1}} - N_{BB_{x-1}} M_B(1-D_B)}{\frac{1}{2} \left\{ M_B(1-D_B) \right\}^2} \delta u. \quad (8)$$

The (BB-AA)_{x-1}BB unit is produced by way of the formation of two bonds. So $D_B = 2u/2M_B$. Now eq. (8) is soluble by means of the sequential operation:

1. for $x = 1$

$$\delta N_{BB_0} = \frac{-2N_{BB_0}}{(1 - D_B)} \delta D_B,$$

which yields

$$N_{BB_0} = M_B (1 - D_B)^2. \quad (9)$$

2. for $x = j$

Let the equation

$$N_{BB_{j-1}} = M_B D_B^{j-1} (1 - D_B)^2 \quad (10)$$

be true for $x = j (\geq 2)$. Then substituting eq. (10) into eq. (8), we have

$$\delta N_{BB_{x-1}} + \frac{2N_{BB_{x-1}}}{1 - D_B} \delta D_B = (x - 1) M_B D_B^{x-2} (1 - D_B)^2 \delta D_B. \quad (11)$$

Multiply both sides of eq. (11) by the integrating factor $\lambda = (1 - D_B)^{-2}$ to yield

$$(1 - D_B)^{-2} \delta N_{BB_{x-1}} + \frac{2N_{BB_{x-1}}}{(1 - D_B)^3} \delta D_B = (x - 1) M_B D_B^{x-2} \delta D_B. \quad (12)$$

Now our equation is exact. Integrating eq. (12), we have

$$N_{BB_{x-1}} = M_B D_B^{x-1} (1 - D_B)^2. \quad (13)$$

Thus eq. (13) is true for all x 's. The probability of finding $(x - 1)$ -mers is then

$$p_{BB_{x-1}} = \frac{N_{BB_{x-1}}}{\sum_{x=1}^{\infty} N_{BB_{x-1}}} = D_B^{x-1} (1 - D_B), \quad (14)$$

where $x = 1, 2, 3, \dots$.

It is more convenient to recast eq. (14) in the form:

$$p_{BB_n} = D_B^n (1 - D_B), \quad (n = 0, 1, 2, 3, \dots). \quad (15)$$

Now eq. (15) represents the distribution of the (BB-AA)_nBB molecules having n AA units.

2.1.2 Molecular Size Distribution in Branching Process

We seek the distribution function of the (BB-AA)_nBB type branched molecules having n R-A_f monomers ($n = 0, 1, 2, \dots$). Consider a tree molecule without rings. This molecule comprises

number of A type molecules :	n	
number of B type molecules :	$\{(f - 1)n + 1\}$	
number of unreacted A FU's :	0	
number of unreacted B FU's :	$\nu_n = g + \{(f - 1)(g - 1) - 1\}n$	
number of reacted A FU's :	$fn (\equiv \text{number of reacted B FU's}).$	(16)

General birth-death formula for n -mers is

$$\delta N_n / \delta u = P_{birth} - P_{death}. \quad (17)$$

The first term of the right hand side represents the birth probability of n -mers and the second term the death probability. The birth-death equation has the analytic expression of the form^{†1}:

^{†1} To check the validity of eq. (18), carry out the summation over all molecular species from $n = 0$ to ∞ to yield:

$$\delta \Omega_0 = \delta \sum_{n=0}^{\infty} N_n = -(f - 1) \delta u,$$

which satisfies the Euler relation: $\Omega_0 = M_B - (f - 1)u$, in support of eq. (18).

$$\frac{\delta N_n}{\delta u} = \frac{\frac{1}{f!} \sum_{\{k_\ell\}=0}^{n-1} \prod_{\ell=1}^f \nu_{k_\ell} N_{k_\ell}}{\frac{1}{f!} \{gM_B(1-D_B)\}^f} - \frac{\frac{1}{(f-1)!} \nu_n N_n \cdot \{gM_B(1-D_B)\}^{f-1}}{\frac{1}{f!} \{gM_B(1-D_B)\}^f}, \quad (18)$$

where the summation of the first term is over all combinations that satisfies $k_1 + k_2 + \dots + k_f = n-1$ along with $0 \leq k_\ell \leq n-1$ ($\ell = 1, 2, \dots, f$). For instance, for the simplest case of $f = 2$, eq.(18) reduces to the familiar form:

$$\frac{\delta N_n}{\delta u} = \frac{\frac{1}{2} \sum_{j=0}^{n-1} \nu_j N_j \cdot \nu_{n-j-1} N_{n-j-1}}{\frac{1}{2} \{gM_B(1-D_B)\}^2} - \frac{\nu_n N_n \cdot \{gM_B(1-D_B)\}}{\frac{1}{2} \{gM_B(1-D_B)\}^2}.$$

Using the equality, $fu/gM_B = D_B$, it is easy to show that $N_0 = M_B(1-D_B)^{\nu_0}$. We expect the solution of eq. (18) is generally of the form:

$$N_k = \frac{M_B}{(f-1)k+1} \omega_k D_B^k (1-D_B)^{\nu_k}, \quad (19)$$

where

$$\omega_k = g \frac{(\nu_k + k - 1)!}{k! \cdot \nu_k!} \quad (k = 0, 1, 2, \dots).$$

Assume that eq. (19) is true for a given k . Then substituting this equation into eq. (18) we have

$$\delta N_n + \frac{\nu_n N_n}{1-D_B} \delta D_B = \frac{g}{f} M_B \sum_{\{k_\ell\}=0}^{n-1} \prod_{\ell=1}^f \frac{1}{(f-1)k_\ell+1} \nu_{k_\ell} \omega_{k_\ell} D_B^{n-1} (1-D_B)^{\nu_n} \delta D_B. \quad (20)$$

Multiplying eq. (20) by the integrating factor, $\lambda = (1-D_B)^{-\nu_n}$, and with the help of the equality

$$\frac{1}{f} \sum_{\{k_\ell\}=0}^{n-1} \prod_{\ell=1}^f \frac{1}{(f-1)k_\ell+1} \binom{\nu_{k_\ell} + k_\ell - 1}{k_\ell} \equiv \frac{1}{(f-1)n+1} \binom{\nu_n + n - 1}{n-1}, \quad (21)$$

we have

$$N_n = \frac{M_B}{(f-1)n+1} \omega_n D_B^n (1-D_B)^{\nu_n}, \quad (19')$$

which is just eq. (19). Thus, since eq. (19) was true for $k = 0$, it is true for all k 's ($k = 0, 1, 2, \dots$). We see that eq. (19) is equal to the cluster distribution function for the multiple link system [3,4], if we simply replace f (functionality of the A type monomer) with J (number of junction points). And for $f = 2$ eq. (19) reduces to the known formula of the R-A_f model. This is the reason why no one has so far addressed the theory of the drop-wise addition polymerization. The analogy between the drop-wise addition polymerization and the multiple link system is, however, only superficial. The situation changes drastically when one takes into consideration the formation of rings.

2.1.3 Distribution of Cyclic Species

Let $C_{f,i} = fM_A/V_A$ be the initial functional unit (FU) concentration of the R-A_f monomer solution before mixing and $C_{g,i} = gM_B/V_B$ the corresponding quantity of the R-B_g monomer solution. In concentrated solutions, we can approximate that all clusters are made up from the tree structure. Suppose an m -tree which has m unreacted A FU's on the root (see Fig. 1). The number of B FU's is then for the x th generation on this tree

$$N(B)_x = (f-m)(g-1) [(f-1)(g-1)D_B]^{x-1}.$$

So, the number of chances, $\phi_{x,m}$, of x -ring formation is

$$\phi_{x,m} = m \times (f-m)(g-1) [(f-1)(g-1)D_B]^{x-1} (1-D_B). \quad (22)$$

Let \mathcal{P} be the probability that one end on an x -chain enters the small volume v around another end on the same chain. Then the velocity of x -ring formation is $\propto \mathcal{P} \phi_{x,m}$, while the velocity of intermolecular reaction is $\propto gM_B(1-D_B) \cdot m(v/V)$. In concentrated solutions, the fraction of an x -ring to be formed for this special tree can be approximated by the relative velocity of the form [4]:

$$\delta N_{R_{x,m}} \cong \frac{\mathcal{P} m (f-m)(g-1) [(f-1)(g-1)D_B]^{x-1} (1-D_B)}{gM_B(1-D_B) \cdot m(v/V)} \delta u. \quad (23)$$

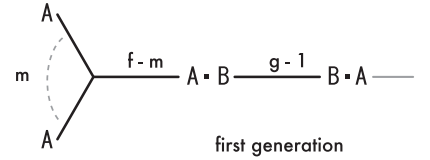


Fig. 1: Representation of an m -tree of the R-A_f + R-B_g branching model.

The total fraction is

$$\sum_{x=1}^{\infty} N_{R_x} = \sum_{x=1}^{\infty} \int_u \sum_{m=1}^{f-1} \delta N_{R_{x,m}} = \sum_{x=1}^{\infty} \int_0^u V \frac{f(f-1)}{2} \frac{\varphi_x(g-1) [(f-1)(g-1)D_B]^{x-1} (1-D_B)}{gM_B(1-D_B)} du, \quad (24)$$

where $\varphi_x = \mathcal{P}/v$. An essential point is that the system volume, V , varies with the advancement of reaction; i.e., the system is diluted successively with the addition of the R-A_f solution. Since the volume element to be added during the unit interval ($\delta u = 1$) is, by definition, $\delta V = V_A/M_A$ and $f u/gM_B = D_B$, the total volume at u is

$$V = \int_0^u (V_A/M_A) du = \left(\frac{gM_B}{fM_A} D_B \right) V_A + V_B, \quad (25)$$

From eqs. (24) and (25) together with $f du/gM_B = dD_B$, we have

$$[F]_{C \rightarrow \infty} = \sum_{x=1}^{\infty} N_{R_x}/V = \chi_1 \sum_{x=1}^{\infty} \varphi_x \frac{1}{2(x+1)} [(f-1)(g-1)D_B]^x + \chi_2 \sum_{x=1}^{\infty} \varphi_x \frac{1}{2x} [(f-1)(g-1)D_B]^x, \quad (26)$$

where

$$\chi_1 = \frac{\gamma_{f,i} D_B}{\gamma_{g,i} + \gamma_{f,i} D_B} \quad \text{and} \quad \chi_2 = \frac{\gamma_{g,i}}{\gamma_{g,i} + \gamma_{f,i} D_B}$$

with $\gamma_{f,i} (= C_{f,i}^{-1})$ and $\gamma_{g,i} (= C_{g,i}^{-1})$ denoting the initial inverse-concentration of respective FU's before mixing. The first term of the right hand side in eq. (26) represents the extra term due to the dilution effect of the drop-wise addition. Hence the conventional homogeneous polymerization is a special case of $\chi_1 = 0$.

2.2 General Drop-wise Addition Polymerization

A more realistic model is that each droplet contains a mass of the R-A_f monomer. Let every droplet contain L R-A_f molecules (L is a large number) which are injected drop-wise onto the R-B_g solution. And consider the case $L \ll N_A$ (Avogadro number), so that each of the R-A_f molecules reacts independently of the others. Assume that the mixing is complete so that the principle of equireactivity is assured.

2.2.1 Size Distribution of Cyclic Species

Consider again a tree with m -unreacted A FU's on the root. The number of B FU's in the x th generation after k drops is then

$$N(B)_x = (f-m)(g-1) [(f-1)(g-1)D_B]^{x-1}, \quad (27)$$

where

$$D_B = \frac{(k-1)fL + f\varepsilon}{gM_B} \quad (0 \leq \varepsilon \leq L, \text{ and } k = 1, 2, \dots). \quad (28)$$

Thus ε expresses the number of R-A_f molecules that reacted in the interval from $k-1$ to k . The number of chances, ϕ_x , of x -ring formation is thus for the m -tree in question

$$\phi_{x,m} = m \times (f-m)(g-1) [(f-1)(g-1)D_B]^{x-1} (1-D_B). \quad (29)$$

The rate of the ring formation can be expressed in the form:

$$v_R \propto \mathcal{P} \sum_{x=1}^{\infty} m \times (f-m)(g-1) [(f-1)(g-1)D_B]^{x-1} (1-D_B) \quad (30)$$

while the rate of intermolecular reaction is

$$v_L \propto m \times gM_B(1-D_B)(v/V). \quad (31)$$

In concentrated solutions, the fraction of rings to be formed per unit reaction ($\delta\varepsilon = 1$) may be approximated as $\delta N_R \cong v_R/v_L$ [4]. By eq. (28), we have $f\delta\varepsilon = gM_B \delta D_B$, which leads to

$$\begin{aligned} \delta N_R &= (V/f) \sum_{m=1}^{f-1} \sum_{x=1}^{\infty} \varphi_x (f-m)(g-1) [(f-1)(g-1)D_B]^{x-1} \delta D_B, \\ &= (V/2) \sum_{x=1}^{\infty} \varphi_x (f-1)(g-1) [(f-1)(g-1)D_B]^{x-1} \delta D_B. \end{aligned} \quad (32)$$

where $\varphi_x = \mathcal{P}/v$. Let $\lambda = fL/gM_B$. Then, with the equality $V = \frac{kL}{M_A}V_A + V_B$ in mind, integrate eq. (32) from $D_B = (k-1)\lambda$ to $k\lambda$ to yield

$$\begin{aligned}\Delta N_R(k) &= (V/2) \sum_{x=1}^{\infty} \int_{(k-1)\lambda}^{k\lambda} \varphi_x (f-1)(g-1) [(f-1)(g-1)D_B]^{x-1} dD_B \\ &= \left(\frac{kL}{M_A} V_A + V_B \right) \sum_{x=1}^{\infty} \varphi_x \frac{1}{2x} [(f-1)(g-1)D_B]^x \Big|_{(k-1)\lambda}^{k\lambda} \\ &= \sum_{x=1}^{\infty} \varphi_x \frac{1}{2x} [(f-1)(g-1)\lambda]^x s(k),\end{aligned}\tag{33}$$

where

$$s(k) = \left(\frac{kL}{M_A} V_A + V_B \right) \{k^x - (k-1)^x\}.\tag{34}$$

The total number of rings accumulated from $k=1$ to n drops is therefore

$$N_R(n) = \sum_{k=1}^n \Delta N_R(k) = \sum_{x=1}^{\infty} \varphi_x \frac{1}{2x} [(f-1)(g-1)\lambda]^x \mathcal{S}(n).\tag{35}$$

Here, the inner sum of the r.h.s. has the form:

$$\begin{aligned}\mathcal{S}(n) &= \sum_{k=1}^n s(k) = \frac{L}{M_A} \{n^{x+1} - (0^x + 1^x + 2^x + \dots + (n-1)^x)\} V_A + n^x V_B \\ &= \frac{L}{M_A} n^x \left(n - \sum_{k=0}^{n-1} (k/n)^x \right) V_A + n^x V_B.\end{aligned}\tag{36}$$

Remark 1: As $n \rightarrow \infty$, eq. (36) can be approximated as

$$\mathcal{S}(n) \doteq \frac{L}{M_A} n^x \left(n - \int_0^n (k/n)^x dk \right) V_A + n^x V_B = \frac{nL}{M_A} \frac{x}{x+1} n^x V_A + n^x V_B.\tag{37}$$

Substituting eq. (37) into eq. (35), we have

$$N_R(n) \doteq \frac{nL}{M_A} V_A \sum_{x=1}^{\infty} \varphi_x \frac{1}{2(x+1)} [(f-1)(g-1)n\lambda]^x + V_B \sum_{x=1}^{\infty} \varphi_x \frac{1}{2x} [(f-1)(g-1)n\lambda]^x.\tag{38}$$

Using the equality, $n\lambda = D_B$, divide eq. (38) by $V(n) = \frac{nL}{M_A} V_A + V_B$ to yield

$$[I] \equiv \frac{N_R(n)}{V(n)} \doteq \chi_1 \sum_{x=1}^{\infty} \varphi_x \frac{1}{2(x+1)} [(f-1)(g-1)n\lambda]^x + \chi_2 \sum_{x=1}^{\infty} \varphi_x \frac{1}{2x} [(f-1)(g-1)n\lambda]^x,\tag{26'}$$

which is just eq. (26). For a large n limit, the general drop-wise addition polymerization converges on the ideal drop-wise addition polymerization.

Remark 2: The physical meaning of eq. (26) is as follows:

1. If $\gamma_{f,i} \gg \gamma_{g,i}$
The R-B_g monomer is, for instance, in non-solvent state, into which the large amount of the R-A_f dilute solution is injected. Thus cyclization occurs mainly due to the dilution effect by the R-A_f solution: $\chi_1 = 1$ and $\chi_2 = 0$.
2. If $\gamma_{g,i} \gg \gamma_{f,i}$
The R-B_g monomer is in dilution state, onto which a small volume of the concentrated R-A_f solution is added. Thus the system approximately retains a constant volume so that $V \cong V_B$ throughout the entire branching process: $\chi_1 = 0$ and $\chi_2 = 1$.

2.3 Gel Point Estimation

The branching probability, α , is defined as the probability that a A FU leads to the next A FU. Let p_{RB} be the fraction of cyclic bonds to all possible bonds for the R-B_g monomer so that $p_{RB} = N_R(D_B)/gM_B$; let p_{RA} be the corresponding quantity for the R-A_f monomer. Fig. 2 shows a typical (BB-AA)_nBB cluster formation from three BB clusters and one R-A₃ monomer ($n = x - 1 + 1 + y + z$). In this case we put unreacted B FU's on the root. Note that cyclization is possible only for unreacted A FU's on the R-A₃ monomer in question which are just added to the system for this unit reaction, contrary to the conventional homogeneous polymerization [4]. α , thus, should be written in the form:

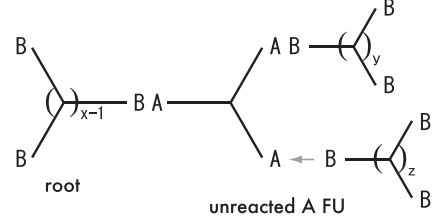


Fig. 2: Representation of a typical n -cluster formation from one R-A_f monomer and three BB clusters.

$$\alpha = D_B \sum_{m=0}^{f-1} m \binom{f-1}{m} \left(1 - \frac{p_{RA}}{D_A}\right)^m \left(\frac{p_{RA}}{D_A}\right)^{f-1-m} (g-1). \quad (39)$$

The gelation occurs at $\alpha = 1$, which, with the equality $\frac{p_{RA}}{D_A} \equiv \frac{p_{RB}}{D_B}$, yields

$$D_{Bc} = \frac{1}{(f-1)(g-1)} + \frac{N_R(D_{Bc})}{gM_B}.$$

For a large n , we can approximate that $N_R(D_{Bc}) \doteq N_R(n_c)$. And we have

$$D_{Bc} \doteq \frac{1}{(f-1)(g-1)} + \frac{N_R(n_c)}{gM_B}. \quad (40)$$

Eq. (40) is of the form:

$$D_{Bc} \equiv D(inter) + D(ring), \quad (41)$$

as expected.

To apply eq. (35) beyond $D_B = D_{Bco}$, expand $N_R(n_c)$ with respect to $D_{Bc} = D_{Bco}$ to yield

$$N_R(n_c) \cong N_R(n_{co}) + \frac{\Delta N_R(n_{co})}{\lambda} (D_{Bc} - D_{Bco}). \quad (42)$$

We introduce the new quantity, the initial dilution ratio $r = \gamma_{f,i}/\gamma_{g,i}$. At $n = n_{co}$, since $n_{co} \lambda (f-1)(g-1) = 1$, we have then

$$\begin{aligned} \frac{\Delta N_R(n_{co})}{\lambda} &= \sum_{x=1}^{\infty} \varphi_x \frac{1}{2x} \left(r + (f-1)(g-1) \right) n_{co} \left\{ 1 - \left(\frac{n_{co}-1}{n_{co}} \right)^x \right\} V_B \\ &\equiv \frac{r + (f-1)(g-1)}{2} \sum_{x=1}^{\infty} \varphi_x \frac{A(x)}{x} V_B; \end{aligned} \quad (43)$$

$$\begin{aligned} N_R(n_{co}) &= \frac{1}{(f-1)(g-1)} \sum_{x=1}^{\infty} \varphi_x \frac{1}{2x} \left\{ r \left(1 - \sum_{k=0}^{n_{co}-1} \frac{k^x}{n_{co}^{x+1}} \right) + (f-1)(g-1) \right\} V_B \\ &\equiv \frac{1}{(f-1)(g-1)} \sum_{x=1}^{\infty} \varphi_x \frac{B(x)}{2x} V_B, \end{aligned} \quad (44)$$

where

$$\begin{aligned} A(x) &= n_{co} \left\{ 1 - \left(\frac{n_{co}-1}{n_{co}} \right)^x \right\}, \\ B(x) &= \left\{ r \left(1 - \sum_{k=0}^{n_{co}-1} \frac{k^x}{n_{co}^{x+1}} \right) + (f-1)(g-1) \right\}. \end{aligned}$$

Substituting eqs. (42)-(44) into eq. (40), we have

$$D_{Bc} = \frac{1}{(f-1)(g-1)} \left\{ \frac{1 - \left(\frac{r + (f-1)(g-1)}{2} \sum_{x=1}^{\infty} \varphi_x \frac{A(x)}{x} - \frac{1}{2} \sum_{x=1}^{\infty} \varphi_x \frac{B(x)}{x} \right) \cdot \gamma_{g,i}}{1 - \frac{r + (f-1)(g-1)}{2} \sum_{x=1}^{\infty} \varphi_x \frac{A(x)}{x} \cdot \gamma_{g,i}} \right\}. \quad (45)$$

Eq. (45) is a general expression of the gel point in the drop-wise addition polymerization. Unfortunately the solution is not very easy to use, since it contains double sum of x and k . So, it is more convenient to approximate eq. (45) by the limiting case of $n = \infty$ (see eq. (46)). Fortunately this is possible, because n is often very large and the difference between eq. (45) and eq. (46) is almost negligible.

Remark 3: As $n \rightarrow \infty$, $A(x) \rightarrow x$ and $B(x) \rightarrow \left\{ r \left(\frac{x}{x+1} \right) + (f-1)(g-1) \right\}$. Then eq. (45) leads to

$$D_{Bc} = \frac{1}{(f-1)(g-1)} \left\{ \frac{1 - \left(\frac{r}{2} \sum_{x=1}^{\infty} \varphi_x \left(1 - \frac{1}{x+1} \right) + \frac{(f-1)(g-1)}{2} \sum_{x=1}^{\infty} \varphi_x \left(1 - \frac{1}{x} \right) \right) \cdot \gamma_{g,i}}{1 - \frac{r + (f-1)(g-1)}{2} \sum_{x=1}^{\infty} \varphi_x \cdot \gamma_{g,i}} \right\}. \quad (46)$$

Now the gel point is a function of the dilution ratio, r , and the initial dilution, $\gamma_{g,i}$. Since r is given as an experimental condition, the gel point is calculable from the first principle.

For $\gamma_{g,i} \gg \gamma_{f,i}$ (that is, for $r \rightarrow 0$), eq. (46) reduces to

$$\lim_{r \rightarrow 0} \text{eq. (46)} \rightarrow D_{Bc} = \frac{1}{(f-1)(g-1)} \left\{ \frac{1 - \frac{(f-1)(g-1)}{2} \sum_x \varphi_x (1 - 1/x) \gamma_g}{1 - \frac{(f-1)(g-1)}{2} \sum_x \varphi_x \gamma_g} \right\}. \quad (47)$$

And in the limit of the infinite concentration, $\gamma_g \rightarrow 0$, we recover the classical relation:

$$\lim_{\gamma_g \rightarrow 0} \text{eq. (46)} \rightarrow D_{Bco} = \frac{1}{(f-1)(g-1)}. \quad (48)$$

3 Comparison with Experiment

To evaluate D_{Bc} as a function of $\gamma_{g,i}$, we must calculate the cyclization frequency: φ_x . In concentrated solutions, we can expect the ideal behavior of branched molecules (no ring formation and no excluded volume), as mentioned earlier [4]. Then φ_x can be expressed by the incomplete gamma function of the form:

$$\varphi_x = (d/2\pi^{d/2} \ell_s^d N_A) \int_0^{d/2\nu_x} t^{\frac{d}{2}-1} e^{-t} dt, \quad (49)$$

where

$$\langle r_x^2 \rangle_{\Theta} = \nu_x \ell_s^2 = C_F \xi_e x \ell_s^2, \quad (50)$$

is the end-to-end distance for an x -chain in the Θ regime; ℓ_s denotes the length (1.37 Å) of the N–C bond in the urea moiety (ℓ_3 in Fig. 3), C_F the Flory characteristic ratio, ξ_e the effective bond number defined earlier [4], and x the number of repeating units.

In this paper, we take up the polyaddition reaction of bis(4-isocyanatocyclohexyl)methane (HMDI: R–A₂ CH₂[(C₆H₁₀)NCO]₂) and poly(oxyalkylenetriamine) (TRI: R–B₃) [1]. To seek the numerical estimate of φ_x , we must determine C_F and ξ_e .

There is little information about the expansion factor of poly(urea). It is important to notice that, according to eq. (46), the location of the gel point depends only on the macroscopic quantity of cyclic species, namely, the total amount, but not on the microscopic detail of the distribution function. As a result, the quantity C_F operates as an adjustment parameter for the total quantity of cyclic species. Then it is readily found through the numerical simulation that when we apply $C_F = 4.5$, close to the value employed to the poly(urethane) homologue, a good result is obtained. The numerical estimate of 4.5 seems reasonable, but it is not yet conclusive; the validity should be verified by another experimental observations.

To calculate the effective bond number, ξ_e , let us examine the stereochemistry of the dicyclohexane moiety on HMDI. There are two known conformations of the cyclohexane ring convertible to each other, the skew and

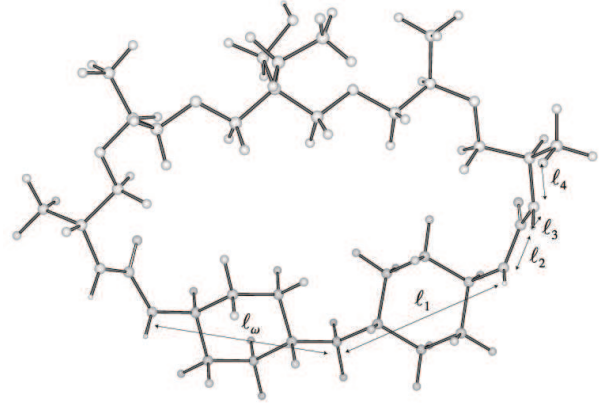


Fig. 3: Representation of the smallest ring to be produced in the polymerization of HMDI and TRI. The dicyclohexane moiety is assumed to take the equatorial-equatorial conformation.

the chair. The chair form represents the lowest energy minimum, while the skew has higher energy because of the presence of the steric hindrance ($\Delta E = 22.6 \text{ kJ/mol}$) due to the two axial 1,4-hydrogen atoms [5], with the statistical weight, $\exp(-\Delta E/RT) \approx 10^{-4}$, showing that the cyclohexane ring exists, in equilibrium, exclusively in the chair form. Then consider the configuration of 1,4-dimethyl cyclohexane. According to the MM2 model calculation, there are three configurational states having energy minima that correspond to: equatorial-equatorial in which the two methyl moieties are splayed out ($\Delta E = 0 \text{ kJ}$), equatorial-axial in which one methyl sticks up or down to the structure and the other is splayed out ($\Delta E = +7.29 \text{ kJ}$), and axial-axial in which both the methyls stick up and down to the structure ($\Delta E = +14.48 \text{ kJ}$). As expected, the equatorial-equatorial configuration is the most stable, and has the statistical weight of 18.68, which amounts to $\approx 95\%$ population of all configurations. Hence we may conclude that the dicyclohexane moiety exists almost exclusively in the equatorial-equatorial configuration.

From the above consideration, we obtain the imaginary bond length, $\ell_1 \simeq 5.83 \text{ \AA}$. Making use of this result, we can determine all the parameters (see Table 1).

Table 1: Parameters for the HMDI-TRI Branched Poly(urea)

parameters	unit	values
Molecular Weight		HMDI = 262
		TRI = 440
f		2
g		3
d		3
C_F		4.5
ξ_c		56
ℓ_s	(\AA)	1.37
Cyclization Frequency	(mol/l)	
$\sum_{x=1}^{\infty} \varphi_x$		0.135
$\sum_{x=1}^{\infty} \varphi_x \frac{1}{x}$		0.069
$\sum_{x=1}^{\infty} \varphi_x \frac{1}{(x+1)}$		0.039

Table 2: Experimental Data in the Drop-wise Addition of HMDI onto TRI [1]

HMDI (mol/l)	[NCO] (equiv/l)	TRI (mol/l)	[NH ₂] (equiv/l)	r dilution ratio	Gel Point (D_{B_c})
0.80	1.60	0.47	1.41	0.88	0.591
0.63	1.26	0.37	1.12	0.89	0.625
0.47	0.93	0.28	0.83	0.89	0.648
0.31	0.61	0.18	0.55	0.90	0.717
0.23	0.46	0.14	0.41	0.89	0.803
0.15	0.30	0.09	0.27	0.90	<i>no gelation</i>

With the help of the parameters of Table 1, together with the observed dilution ratio, $r = \gamma_{f,i}/\gamma_{g,i} = 0.89$ (Table 2), we can plot eq. (46) as a function of $\gamma_{g,i}$. In Fig. 4, open circles represents experimental points by Unal and coworkers, and the solid line the theoretical line by eq. (46). The general trend of the theory is in good accord with the observations.

4 Discussion

4.1 Interpretation of Results

As one can see, however there is appreciable numerical difference between the theory and the experiments. Fortunately this can be explained on the basis of (i) side reactions and (ii) deviation from the basic assumptions.

It has been known earlier that isocyanates ($-\text{NCO}$) can react with alcohols ($-\text{OH}$) to form urethane bonds ($-\text{NHCOO}-$). Hence, in the system cited above [1], the poly(urea) formation must always be accompanied by the urethane bond formation that wastes FU's because of the use of isopropyl alcohol as the reaction solvent. This necessarily shifts the gel point upwards. In light of the observations [6] of the cyclotrimerization of bisphenol-A dicyanate^{†2}, it is probable that the alcoholysis of HMDI as a side reaction causes most of the discrepancy in question.

There might be other factors that cause the deviation. For instance, the theory has been derived on the assumption that the mixing is sufficient to assure the principle of equireactivity, while a set of reactions (1)-(3) must be completed within the minute interval of the unit cycle, so that the system always comprises $(\text{BB-AA})_n\text{BB}$ type molecules alone. This poses a problem because the system has to obey, on one hand, a very slow reaction with respect to the realization of the sufficient mixing; it has to obey, on the other hand, a very fast reaction with respect to the instantaneous completion of the reaction cycle (1)-(3); it is clear that a delicate balance is required to realize a genuine drop-wise polymerization, deviation from which should shift the gel point upwards.

Taking these circumstances into consideration, it is by no means unreasonable to conclude that there is a satisfactory agreement between the theory and the experiments.

4.2 Comparison with Conventional Branching Process

It will be of interest to inquire the question, 'If all R-A_f molecules are added at once, where is the gel point observed?' The gel point in that conventional polymerization has been found to obey the equation [4]:

$$D_{A_c} = \sqrt{\frac{1}{s}} \left\{ \frac{1 - (1 + \kappa) \sqrt{s} \sum_x (1 - 1/2x) \varphi_x \gamma}{1 - (1 + \kappa) \sqrt{s} \sum_x \varphi_x \gamma} \right\}, \quad (51)$$

where $s = (f - 1)(g - 1)/\kappa$, $\kappa = gM_B/nfL$ (≥ 1) as defined earlier, and $\gamma^{-1} = \frac{nfL + gM_B}{V}$. κ corresponds to the reciprocal of the gel point in the drop-wise addition polymerization. By eq. (25) we have $V = V_B(1 + r/\kappa)$. Substituting this into eq. (51) together with some rearrangement, we have

$$D_{B_c} = \sqrt{\frac{1}{s'}} \left\{ \frac{1 - (1 + r/\kappa) \sqrt{s'} \sum_x (1 - 1/2x) \varphi_x \gamma_{g,i}}{1 - (1 + r/\kappa) \sqrt{s'} \sum_x \varphi_x \gamma_{g,i}} \right\}, \quad (52)$$

where $s' = \kappa(f - 1)(g - 1)$, and $r = \gamma_{f,i}/\gamma_{g,i}$ and $\gamma_{g,i}$ the reciprocal of the initial B FU's concentration before mixing as defined in the text. Physically, D_{B_c} in eq. (52) must be less than $1/\kappa = nfL/gM_B$ (the gel point in the drop-wise addition polymerization), because exactly nL R-A_f molecules are mixed at once with M_B R-B_g molecules. The calculation of eq. (52) showed that $D_{B_c} = 0.595$ for $1/\kappa = 0.591$, 0.632 for $1/\kappa = 0.625$ and so forth. It was found that for all examples, the gel points (D_{B_c}) of the conventional polymerization exceed those ($1/\kappa$) of the drop-wise addition polymerization. This indicates that the gelation will never occur in the conventional polymerization if the reaction is carried out under the same conditions as those employed in the drop-wise addition polymerization. In order for the gelation to occur, more concentrated circumstances are needed. In other words, in the drop-wise addition polymerization, the system behaves as if the cyclization is less frequent than in the conventional branching process.

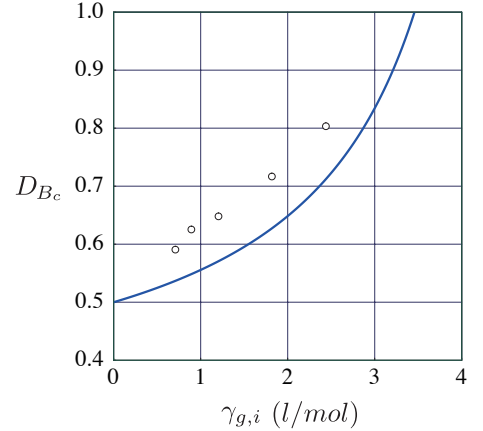


Fig. 4: Concentration dependence of gel points in the drop-wise addition reaction for $f = 2$, $g = 3$. \circ : observed points by Unal and coworkers [1]; solid line (—): theoretical line by eq. (46).

^{†2} There is a good example of the effect of side reactions on the shift of gel points [6]. The presence of H_2O moisture in the reactor is known to cause the hydrolysis of bisphenol-A dicyanate leading to the complicated side reactions and shifts the gel point upwards to a large extent, from the correct value 0.508 to 0.6 or higher values.

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